space group. The X-ray scattering properties of scandium, make scandium manganese(III) oxide more suitable for obtaining accurate information of the crystal structure type of these compounds and a determination of the crystal structure of scandium manganese(III) oxide is in progress.

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On the First, Naturally Occurring Amino Tricarboxylic Acid, Isolated from the Mushroom *Lactarius helvus*

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In the course of studies [1-3] on the soluble nitrogen compounds in the mushroom *Lactarius helvus*, a new amino acid, formerly called amino acid B, has been isolated in pure form and characterized in some detail. This compound, which on the paper chromatogram gives a yellow-brown spot with ninhydrin, was shown to be acidic on the basis of its mobility at pH 5.6 on paper electrophoresis.[1]

The isolation of the amino acid B was performed in a similar manner to that described earlier by Casimir and Virtanen.[1] It was separated moderately well from the other amino acids on a Dowex-1 column using 1 N acetic acid as eluant instead of 1 N hydrochloric acid.[1] After further purification on a cellulose powder column, eluting with BuOH:AcOH:H_2O (12:3:5), the amino acid B was crystallized from a mixture of BuOH-EtOH-H_2O by evaporating off the ethanol and water slowly at reduced pressure. The compound B has no defined melting point, but begins to darken and decompose above 200°C. Elementary analysis gave the empirical formula $C_{12}H_{17}NO_7$. (Found: C 48.50; H 5.83; N 4.98; O 39.67. Calc. for $C_{12}H_{17}NO_7$ (287.26): C 50.17; H 5.97; N 4.88; O 39.99). An α-amino and neighbouring carboxyl group determination according to Linko [4] gave the following values: N 4.7; CO_2 15.8. Calc. for $C_{12}H_{17}NO_7$: N 4.88; CO_2 (for one carboxyl group) 15.35. A titration of the compound B in ethanol with ethanolic sodium hydroxide (phenolphthalein as indicator) gave an equivalent weight of 96.5. If we assume that the molecule contains three carboxyl groups, the equivalent weight would be 287.26/3 = 95.75. On catalytic hydrogenation one mole of hydrogen was consumed per mole of the amino acid B. The compound B shows no absorption in the UV-region, so that the double bond is not conjugated with the carboxyl groups. No keto group was present. The empirical formula $C_{12}H_{17}NO_7$ shows that the molecule must contain a ring, since only one double bond is present.

On the basis of the NMR-spectra, the original amino acid B and its hydrogenation product contain no methyl group, but two olefinic protons are, however, discernible. A peak occurs in the area expected for a proton on a carbon atom attached a carboxyl group $H-\underset{|}{\overset{|}{C}}-COOH$.

The mass spectrum of a derivative of the amino acid B, which was obtained by the conversion of the amino group to a hydroxyl group with nitrous acid followed by treatment with diazomethane, is presented in Fig. 1. As can be seen, the highest mass number occurs at m/e = 312. If we assume that all the three carboxyl groups have been esterified and the amino group exchanged for a hydroxyl group, the derivative would have a molecular weight of 330 ($C_{15}H_{22}O_8$). The difference between the values of 330 and 312 is 18 mass units. It is, however, very common that organic molecules containing hydroxyl groups have no molecular peak in their mass spectra because of the ease of elimination of water from the molecular ion.

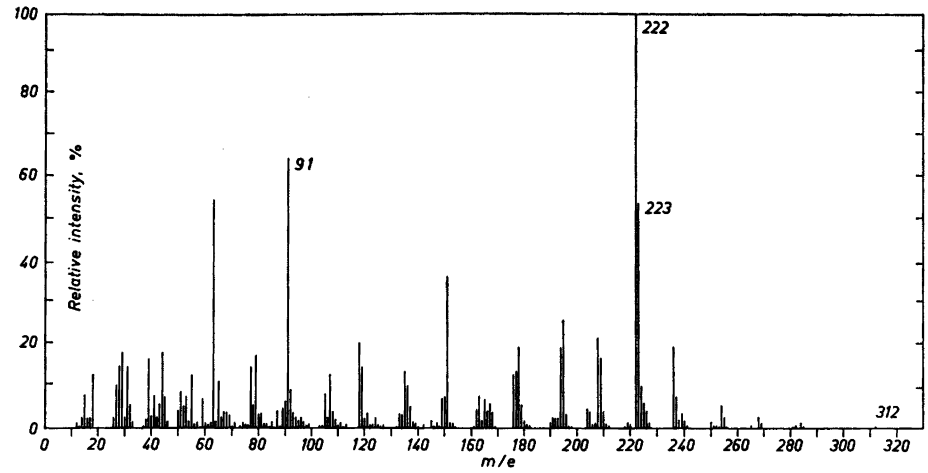

Fig. 1. Mass spectrum of a derivative of amino acid B, which was obtained by the conversion of the amino group to a hydroxyl group with HNO_2 followed by treatment with CH_2N_2.

The formation of the peak pair at m/e = 222 and 223 can be interpreted by the loss of $CHOH-COOCH_3 + H^{\cdot}$ and $CHOH-COOCH_3$ from the fragment ion at m/e = 312, respectively. The occurrence of an intense peak having such a large mass number (m/e = 222) is a proof of a strongly conjugated ring structure for this fragment ion. The third strong peak at m/e = 91, the so-called tropylium ion ($C_7H_7^+$), which is typical of many aromatic compounds, indicates probably a seven-membered ring structure in this case.

Because of these results and the analogy between the two compounds it is possible that the amino acid B has the same carbon skeleton as amino acid A isolated in this laboratory also from the mushroom *Lactarius helvus*. For this compound we have earlier proposed the structure of 2-methylene cycloheptene-1,3-diglycine.[3] If in this molecule the methylene group were oxidized to the third carboxyl group, and one of the amino groups exchanged with a hydroxyl group we would arrive at the structure of amino acid B. This amino acid would thus contain one double bond in a seven-membered ring with $CH_2(NH_2).COOH$, COOH and $CH_2(OH).COOH$ attached to the ring. As far as the authors are aware, no other tricarboxylic amino acid has earlier been found in nature.

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